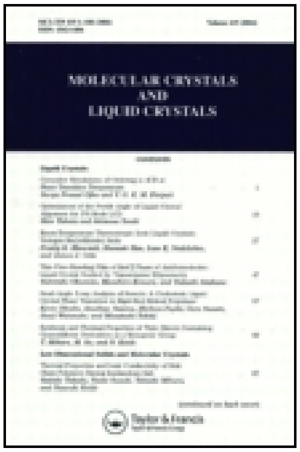

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Yu. V. Malyukin [a] , O. G. Tovmachenko [a] , G. S. Katrich [a] , S. L. Efimova [a] & K. Kemnitz [b]

[a] Institute of the Single Crystals of National Academy of Sciences of Ukraine, 60 Lenin Ave., 310001, Kharkov, Ukraine Phone: 38 0572 30-70-49 E-mail:

[b] EuroPhoton GmbH. 27, Mozart str., D-12247, Berlin, Germany Phone: 49 30 77790145 E-mail:

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Exciton Trapping Mechanism in Quasi-1D Molecular Chains (J-aggregates)

YU. V. MALYUKIN, O. G.TOVMACHENKO, G. S.KATRICH,
S. L. EFIMOVA, K. KEMNITZ*
Institute of the Single Crystals of National Academy of Sciences of Ukraine,
60 Lenin Ave., 310001, Kharkov, Ukraine,
phone: 38 (0572) 30-70-49, e-mail:malyukin@isc.kharkov.ua
* EuroPhoton GmbH. 27, Mozart str., D-12247 Berlin, Germany,
phone: 49 30 77790145, e-mail: 100520.3341@compuserve.com

The exciton trapping mechanism by impurity centers in quasi-1D molecular chains (J-aggregates) is studied for the binary solutions of dimethylformamide and water. It is determined that the exciton energy transfer is occurring due to the dipole-dipole mechanism. The influence of the exciton self-trapping process on the trapping efficiency was found. It is shown that the exciton trapping occurs mainly owing to free excitons. The critical radius and trapping rate were determined.

Keywords: J-aggregate, exciton, exciton trapping.

Traditionally, one of the efficient methods of gaining information about exciton transport in low-dimensional systems is study of exciton trapping by impurity centers. This method is of an additional interest for the present work due to the observed exciton self-trapping in J-aggregates [1]. The appearance of an additional competing channel of non-radiative relaxation should affect the exciton trapping mechanism.

The present work studies the J-aggregates of 1-methyl-1'-octadecyl-2,2'-cyanine iodide (S120) having the exciton traps. The formation of J-aggregates occurred in the binary solutions of dimethylformamide (DMF) and water, according to[1]. 1,1'-dioctadecyl-2,2',3,3'-tetramethylindodi-carbocyanine perchlorathe (D307) molecules were used as the exciton traps. Choosing these molecules as the traps is explained by several reasons. First, D307 molecules belong to the same class of luminophors as S120 ones and have a similar structure. On the other hand, in binary solution of DMF-water, luminescence quenching of D307 molecules takes place.

The initial solutions of S120 and D307 molecules in DMF were preliminary mixed in certain proportion to form the aggregate-trap system. The concentration of D307 molecules relative to S120 molecules was of 1:500. The absorption and luminescence spectra of this solution are the additive set of absorption and luminescence curves of S120 and D307 molecules in DMF (Fig. 1a, 2a).

Further, the distilled water was added to the obtained solution for S120 J-aggregates formation. In the luminescence spectrum of the binary solution with a low (50%) percentage of water a significant D307 molecules luminescence buildup observed (Fig. 2b). However, D307 molecule absorption against the background intensive J-band is not seen (Fig. 1b) due to their low concentration $C_{D307}=10^{-7}$ M. On the other hand, in a similar binary solution but with higher concentration of $C=5x10^{-5}$ M containing D307 molecules only, a complete quenching of their luminescence was seen (Fig. 1c). Consequently, when S120 J-aggregates are present, D307 molecule luminescence buildup in binary solution arises from the exciton trapping by these molecules followed by their radiative relaxation.

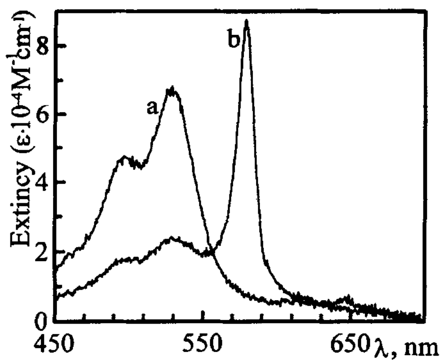

FIGURE 1. Absorption spectra of the compound S120+D307=500:1, at 300K: a) in DMF; b) in a binary solution (50% water).

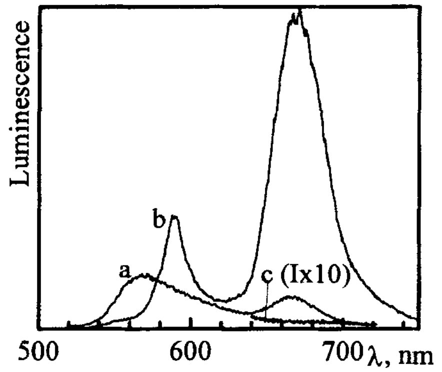

FIGURE 2. The luminescence spectra of the compound S120+D307=500:1, at 300K: a) in DMF; b) in a binary solution (50% water); c) D307 in a binary solution (50% water).

The luminescence decay of D307 molecules in DMF at T=293K is described by the single exponential law, with the lifetime of 1.7 nsec. On the contrary, the luminescence decay of a binary solution with S120 J-aggregates and traps recorded in the trapping band has nonexponential behavior (Fig. 3a). In the last case the leading edge of kinetics is displaced relative to the laser impulse one, while they coincide when S120 J-aggregates are absent. This fact additionally confirms the presence of exciton trapping by D307 molecules. The position of the luminescence kinetics maximum in the trapping band changes with the temperature decrease to 1.5K (Fig. 3b).

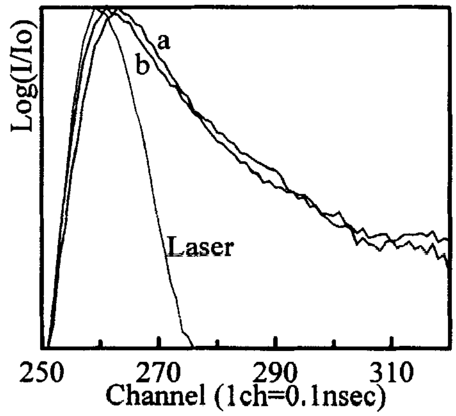

FIGURE 3. The luminescence decay in a trapped band:
a) T=300K; b) T=1.5K.

The populations in the exciton N_{ex} and trap N_{tr} band are described by the following equations:

$$\begin{cases} \frac{dN_{ex}}{dt} = -(K_{ex}^R + K_{tr} + K_{str})\cdot N_{ex} \\ \frac{dN_{tr}}{dt} = -K_{tr}^R \cdot N_{tr} + K_{tr}\cdot N_{ex} \end{cases} \qquad (1)$$

where K_{ex}^R is the exciton radiative rate, K_{tr}^R is the trap radiative rate, K_{tr} is the exciton trapping rate, K_{str} is the exciton self-trapping rate.

We have established that K_{ex}^R varies with temperature from $3x10^9$ at 300K to $1.2x10^{10}$ at 1.5K, while K_{tr}^R remains constant within this temperature range at $1.5x10^9$. As to the rate constant K_{str} allowing for self-trapping of excitons, we failed to find its accurate quantitative estimates. The approximation of the luminescence decay curves for the trap band by fitting the K_{tr} value in the solution of Eq.(1) demonstrates that satisfactory agreement can be achieved solely at the initial portion of the decay curve. The best fit of the experimental curves at 300K is achieved at $K_{tr}=2.6\mathrm{x}10^{11}$ sec^{-1}. At 1.5K we have $K_{tr}=3.7\mathrm{x}10^{11}$ sec^{-1}. We presume that the changes in K_{tr} are caused by alterations in the microscopic nature of exciton transport which with lowering temperature acquires more pronounced coherent properties.

At the microscopic level the solvate shell of S120 J-aggregates in a binary solution, has evidently the following structure: J-aggregates themselves are predominantly surrounded with water molecules and the region of the space occupied by the $C_{18}H_{37}$ radicals of S120 molecules producing mostly J-aggregates contains DMF molecules. Localization of D307 molecules possessing two water-insoluble radicals $C_{18}H_{37}$ near a J-aggregate in the region occupied by radicals of S120 molecules is energetically favorable. However, D307 molecules cannot be incorporated directly in the J-aggregate chain because of considerable sterical hindrance.

The energy transfer from S120 J-aggregates to traps occurs due to the dipole-dipole mechanism. We can evaluate the transfer critical radius basing on the relationship:

$$R_0 = \sqrt[6]{\frac{9000\cdot \mathrm{Ln}(10)\cdot k^2\cdot \varphi_J}{128\cdot \pi^5\cdot n^4\cdot N_A}\cdot \gamma}\ , \qquad (2)$$

where k^2 is the factor describing the dipole mutual orientation; n is the solvent refraction index; N_A is the Avogadro constant; φ_J is the J-aggregates luminescence quantum yield; γ is the overlapping integral of J-aggregates luminescence and the traps absorption spectra. Substituting $n=1.41$, $\varphi_J=0.11$ in

Eq.(2), and calculating the overlapping integral $\gamma \sim 10^{-14}$ cm^3/M using experimental spectra, as well as substituting k^2 with its average value, we obtain the critical radius value $R_0 = 11\ \overset{o}{A}$. The above estimated R_0 is comparable with the characteristic size of D307 localization regions in the J-aggregates neighborhood.

Cooling the investigated binary solution with the 50% water content down to the temperature of 1.5K yields the trap luminescence intensity decrease (Fig. 4b). Simultaneously the characteristic asymmetric broadening of the S120 J-aggregates luminescence band in long-wave region of spectrum dye to exciton self-trapping was observed[1]. It should be noted that if the traps were absent the peak intensity of luminescence bands both for the free and self-trapped excitons were equal (Fig. 4a). However, the peak intensity of self-trapped exciton luminescence band 3 time exceeds that of the free exciton one when the traps are present (Fig. 4b). The latter takes the shape of a narrow short-wave shoulder in the luminescence spectrum, which is shown in Fig. 4b. It is shown that the exciton trapping occurs mainly owing to free excitons.

The drop in luminescence intensity of traps on the temperature decrease was previously observed in[2] for J-aggregates in LB-films and interpreted by the reduction of the exciton lifetime. In our case, the exciton lifetime reduction is also seen on the temperature decrease. However, an alternative contribution to the drop of the luminescence intensity in a trapping band will yield the exciton self-trapping decrease in their mobility and respectively of capture on traps.

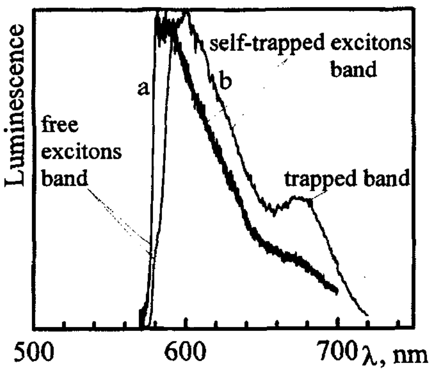

FIGURE 4. Luminescence spectra S120 J-aggregates in a binary solution (50% of water) at 1.5K: a) traps are absent; b) traps are present.

Thus, we have demonstrated that D307 molecules in binary solution DMF-water containing S120 J-aggregates play the role of traps for excitons. The exciton energy transfer occurs due to the dipole-dipole mechanism. The influence of the exciton self-trapping process on the trapping efficiency has been found. The exciton trapping occurs mainly owing to free excitons.

Acknoledgments

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